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Monsanto Research Corp, Dayton, OH

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Status Assessment of Toxic Chemicals

Vinylidene Chloride

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16. ABSTRACT

This report details the uses and the technology employed to control emissions of vinylidene chloride. Data on vinylidene chloride emissions and their sources are given, as well as information dealing with the effects of exposure to vinylidene chloride. Finally, regulatory actions and areas requiring further study are outlined.

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Please change the following:

page iii, paragraph 2, line 3, from "asbestos" to "vinylidene chloride."

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STATUS ASSESSMENT OF TOXIC CHEMICALS:
VINYLIDENE CHLORIDE

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains a status assessment of the air emissions, water pollution, health effects, and environmental significance of asbestos. This study was conducted to provide a better understanding of the distribution and characteristics of this pollutant. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

Status assessment reports are used by IERL-Ci to communicate the readily available information on selected substances to government, industry, and persons having specific needs and interests. These reports are based primarily on data from open literature sources, including government reports. They are indicative rather than exhaustive.

David G. Stephan
Director
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ABSTRACT

Vinylidene chloride (VDC) is synthesized from ethylene dichloride with 109 x 10^3 metric tons produced annually. VDC monomer is used in the manufacture of barrier coatings, fibers, and plastics. It is estimated that 1.0 x 10^3 to 1.8 x 10^3 metric tons/yr of vinylidene chloride are emitted to the atmosphere from VDC production and consumption.

Control technology for VDC production includes activated carbon adsorption, refrigerated solvent scrubbing, incineration, and vent recovery systems. Technology effective in controlling vinyl chloride emissions is applicable to VDC; industry is therefore adopting similar controls.

Exposure to vinylidene chloride may cause adverse effects to the central nervous system and liver functions of humans. Recent studies have indicated that a high percentage of workers exposed to chronic levels of VDC have shown a substantial loss in liver function. NIOSH is planning to evaluate further studies to determine what workplace standards should be adopted.

The quantity and composition of organic pollutants from plants where VDC is produced or consumed was not available for this report. Quantitative analysis and assessment of pollutants from plants where VDC is used needs to be accomplished to determine the potential health hazards of VDC production and consumption to surrounding populations.

This report was submitted in partial fulfillment of Contract 68-02-2550 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1, 1977 to December 31, 1977. The work was completed as of January 20, 1978.

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CONVERSION FACTORS AND METRIC PREFIXES[a]

CONVERSION FACTORS

To convert from	to	Multiply by
Degree Celsius (°C)	Degree Fahrenheit	$t_F^\circ = 1.8\ t_C^\circ + 32$
Kilogram (kg)	Pound-mass (pound-mass avoirdupois)	2.204
Kilometer^2 (km^2)	Mile^2	3.860×10^{-1}
Meter^3 (m^3)	Foot^3	3.531×10^{1}
Meter^3 (m^3)	Gallon (U.S. liquid)	2.642×10^{2}
Metric ton	Pound-mass	2.205×10^{3}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^3	1 kg = 1×10^3 grams
Milli	m	10^{-3}	1 mm = 1×10^{-3} meter

[a] Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^\epsilon$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

ACKNOWLEDGEENT

This report was assembled for EPA by Radian Corporation, Austin, TX, and Monsanto Research Corporation, Dayton, OH. Mr. D. L. Becker served as EPA Project Officer, and Dr. C. E. Frank, EPA Consultant, was principal advisor and reviewer.

SECTION 1

INTRODUCTION

Vinylidene chloride (VDC) is an important monomer in the manufacture of methyl chloroform, saran, and other plastics. In January, 1976, The National Institute of Occupational Safety and Health (NIOSH) reported that about 60% of workers examined in a New Jersey plant using VDC had developed liver disorders and announced its intention to investigate the situation. Previous laboratory animal studies had suggested that VDC might be a liver carcinogen and might produce a number of other adverse health effects.

This report briefly describes the production and environmental release of VDC. Potential human exposure and health effects due to VDC exposure are also given. Present and future control technology for VDC emissions are explained along with government regulatory actions.

SECTION 2

SUMMARY

The manufacture of vinylidene chloride (VDC) is commercially significant, with an annual production level of 109×10^3 metric tons[a]. End uses of vinylidene chloride include polymerization of the monomer to form barrier resins used in film coating and the fabrication of various packaging materials. Approximately 80% of the vinylidene chloride produced is used captively to produce 1,1,1-trichloroethane or in polymer synthesis.

Emissions of VDC adversely affect humans. Exposure to VDC causes central nervous system depression, skin and eye irritation, and altered liver function. VDC is also a suspected carcinogen. It has been estimated that 1.0×10^3 to 1.8×10^3 metric tons/yr of vinylidene chloride are emitted to the atmosphere from VDC synthesis and polymerization and from polymer fabrication. Within a 5-mile radius of all plants where VDC is produced or used, there are 3.6 million persons who may be exposed to VDC emissions.

Control technology for VDC emissions during production include activated carbon adsorbers, refrigerated solvent scrubbing systems and incinerators. Storage tank emissions are controlled by refrigerated vent recovery systems or return venting to main process streams. Workers at industrial sites where VDC is made or used have the greatest risk from exposure. Careful plant maintenance and handling procedures are mandatory precautions to ensure a reasonably safe work environment.

A workplace standard may be recommended by the National Institute of Occupational Safety and Health (NIOSH). Preliminary studies have indicated that VDC regulation under the Clean Air Act is not warranted at this time.

Table 1 summarizes major points of information given in the report on production, transportation, and uses of VDC.

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[a] 1 metric ton = 10^6 grams; conversion factors and metric system prefixes are presented in the prefatory pages of this report.

TABLE 1. VINYLIDENE CHLORIDE

Emission source	Extent of problem: Emission quantity, metric tons/yr	Extent of problem: Population exposed, persons	Control method	Regulatory action
Production:				
From ethylene dichloride	1.5×10^3	89,000	Carbon adsorbers, refrigerated solvent scrubbing, incineration, refrigerated vent recovery systems, controls similar to vinyl chloride control.	Regulation under Sections 111 and 112 of Clean Air Act not needed at this time. TLV - 40 mg/m^3. Designated as a priority pollutant under the Federal Water Pollution Control Act.
Transportation:				
Vehicle loading and cleaning	0.3×10^3[a]	_[b]	Purge lines to carbon adsorption unit or incinerator.	Tank car size has been limited to 95 m^3.
Industrial use:				
Consumption, 1974	0.3×10^3[a]	3,500,000	_[b]	Workplace standards may be recommended.
18×10^3 metric tons/yr	_[b]	_[b]	_[b]	
polymerization	_[b]	_[b]	_[b]	
fabrication				

[a] Value represents the mass of emissions for both transportation and industrial use.

[b] Information unknown.

Based on the information provided in this report, the following items should be considered in future studies:

- Environmental levels of VDC.
- Quantity and composition of emissions from the polymerization and use of VDC polymers in fabricated products.
- Amount of VDC and related compounds discharged to waterways.
- The effectiveness and cost of control technology applicable to VDC production and consumption facilities.
- Chronic effects of prolonged low level exposure to VDC.

Due to the demonstrated toxicity of VDC, it is recommended that VDC emissions be regulated from plants where VDC is produced or consumed. Imposed regulations need to be based on health effects data and pollutant assessments from VDC plants. Acceptable environmental levels of VDC need to be defined.

SECTION 3

SOURCE DESCRIPTION

CHEMICAL AND PHYSICAL PROPERTIES

The chemical name for VDC is 1,1-dichloroethylene and its molecular formula is $CH_2=CCl_2$. The properties of VDC are listed in Table 2.

TABLE 2. CHEMICAL AND PHYSICAL PROPERTIES OF VDC (1)

Molecular weight:	97.0	Physical state:	Volatile liquid
Vapor pressure:	82.28 kPa at 25°C	Melting point:	-122.53°C
Boiling point:	37°C at 101.33 kPa	Solubility:	Insoluble (H_2O)
Density:	1.213 at 20°C/4°C		

The flash point of VDC is about -10°C, but it will not support combustion. The explosive limit range is 7 to 16 volume percent in room temperature air.

VDC polymerizes spontaneously within 48 hours of production. If it is stored, small amounts of polymerization inhibitors (hydroquinone, alkylamines, or organic sulfur derivatives) are added (2). If VDC is stored in the presence of air or oxygen without an inhibitor at temperatures in the range of -40°C to +25°C, the oxygen dissolves and reacts quickly to form a peroxide compound. The peroxide compound is violently explosive. It is adsorbed on the polymer and any separation (i.e., degradation) of this polymer will result in an explosive compound. A slight mechanical shock or heat will detonate a dry compound containing more than 15% of the peroxide (1). A typical analysis of commercial grade VDC is shown in Table 3.

---

(1) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 21. John Wiley and Sons, Inc., New York, New York, 1970. pp. 275-279.

(2) Hushon, J. and M. Kornreich. Air Pollution Assessment of Vinylidene Chloride. MTR-7230. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1976. 73 pp.

The slow decomposition of VDC peroxides will produce formaldehyde, phosgene, and hydrochloric acid. A sharp acrid odor probably indicates the presence of peroxides (1). The atmospheric reactivity of VDC is given in Table 4 (3).

TABLE 3. TYPICAL ANALYSIS OF VDC (1)

Constituent, ppm[a]	Value
Vinylidene chloride,[b] wt%	99.7
Vinyl chloride	850
cis-1,2-dichloroethylene	500
trans-1,2-dichloroethylene	1,500
1,1-Dichloroethane	10
Ethylene dichloride	10
1,1,1-Trichloroethane	150
Trichloroethylene inhibitor	10
MEHQ[c] grade	200
Phenol grade, wt%	0.6 to 0.8

[a] Except where indicated.

[b] Excluding inhibitor.

[c] Monomethyl ether of hydroquinone.

TABLE 4. ATMOSPHERIC REACTIVITY OF VDC TO ATMOSPHERIC RADICALS (3)

Activity towards radical	Half life
Ozone	<1 day
Ketone	>1,000 days
Hydroxyl	<1 day, producing phosgene and formaldehyde

PRODUCTION

Vinylidene chloride is produced at three locations with a total estimated production of 109 x 10^3 metric tons/yr. Table 5 identifies manufacturers and estimated production levels.

The chlorination of ethylene dichloride produces 1,1,2-trichloroethane and it is estimated that the use of ethylene dichloride

(3) Dorigan J. Scoring of Organic Air Pollutants: Chemistry, Production, and Toxicity of Selected Synthetic Organic Chemicals. Mitre Corporation, September, 1976.

for the production of VDC will increase at an average annual rate of 7% from 1974 to 1979. It is also estimated that the consumption of methyl chloroform, used in the other VDC production method, will not change over this time period.

TABLE 5. VDC PRODUCTION LOCATIONS (1974)

Producer	Location	Production, 10^3 metric tons/yr
Dow Chemical, Co.	Freeport, TX Plaquemine, LA	64[a]
PPG Industries, Inc.	Lake Charles, LA	45[b]
TOTAL		109

[a] Dow was planning to expand plant capacity during 1975.

[b] Approximately 32 x 10^3 metric tons (70%) of this VDC production were used to manufacture 1,1,1-trichloroethane.

PROCESS DESCRIPTION

Vinylidene chloride (VDC) is made from ethylene dichloride. Intermediates may be 1,1,1-trichloroethane (methyl chloroform) or 1,1,2-trichloroethane. In addition, VDC is used to manufacture methyl chloroform only when the VDC has been produced from 1,1,2-trichloroethane. The actual amount of VDC produced and consumed is unknown; however, 77 x 10^3 metric tons is ultimately produced. An additional 32 x 10^3 metric tons is estimated to be formed as an intermediate to methyl chloroform. The reversible reaction for the formation of VDC from methyl chloroform is (4):

$$CH_3CCl_3 \longrightarrow CH_2{=}CCl_2 + HCl \qquad (1)$$

methyl chloroform — vinylidene chloride — hydrochloric acid

VDC is also made by dehydrochlorinating 1,1,2-trichloroethane with lime or aqueous sodium hydroxide, as shown in Equation 2 (4).

$$CH_2ClCHCl_2 + NaOH \longrightarrow CH_2{=}CCl_2 + NaCl + H_2O \qquad (2)$$

1,1,2-trichloroethane + sodium hydroxide — VDC + sodium chloride + water

This reaction takes place at approximately 70°C in a long cylindrical reaction vessel. The crude product is separated by distillation under a nitrogen atmosphere. A phenolic inhibitor is

(4) Sherwood, P. W. Raw Materials for Plastics and Resins. Industrial and Engineering Chemistry, 54(12):30, 1962.

generally added to the distilled product. Product VDC is purified by washing with ferrous sulfate and caustic soda solution. After washing, inhibited vinylidene chloride is dried by azeotropic distillation and sent to a finishing column where purified vinylidene chloride is withdrawn and stored. More inhibitor may be added prior to storage (2). Figure 1 is a flow diagram showing the production and purification of vinylidene chloride (2, 5).

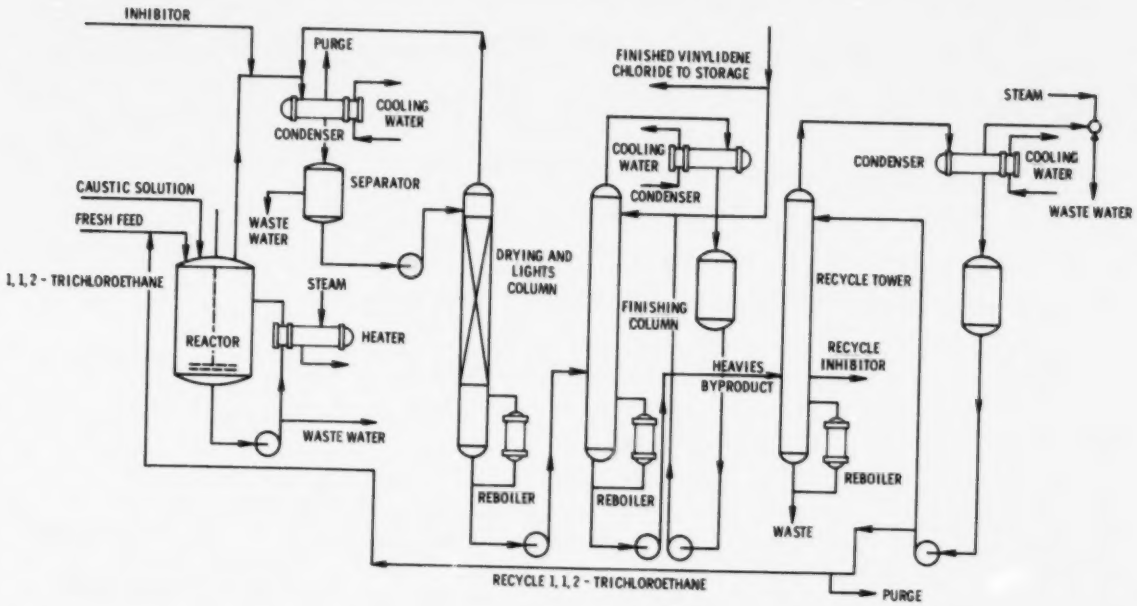

Figure 1. Flow diagram showing the production and purification of vinylidene chloride (2, 5).

Vinyl and Diene Monomers, Copyright (C) 1971.
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USES

It is estimated that 70% of the VDC produced by PPG Industries is used captively to make 1,1,1-trichloroethane. Dow Chemical also captively uses about 78% of its VDC in polymer synthesis (6). The remaining VDC (18 x 10^3 metric tons/yr) is marketed to a variety of secondary users.

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(5) Shelton, L. G., D. E. Hamilton and R. H. Fisackerly. Vinyl and Vinylidene Chloride. In: Vinyl and Diene Monomers, Part 3, Volume 24. E. C. Leonard, ed. Wiley, Interscience, New York, New York, 1971. pp. 1205-1282.

(6) Landau, E., and N. E. Manos. Epidemiology Studies, Task IV Vinylidene Chloride. EPA-560/6-76-022, U.S. Environmental Protection Agency, Washington, D.C., August 1976. 128 pp.

VDC is consumed in the production of films, fibers, plastics, and paper coatings (7). The manufacture of polyvinylidene copolymers is the major use of VDC. The extruded films of the copolymers are used in packaging and have excellent resistance to water vapor and most gases (1). The chief copolymer is Saran (polyvinylidene chloride/vinyl chloride), a transparent film used for food packaging. The films shrink when exposed to higher than normal temperatures. This characteristic is advantageous in the heat-shrinking of overwraps on packaged goods and in the sealing of the wraps (1). Recent growth in the production of shrinkable bags from the VDC copolymer, vinyl chloride/VDC/vinyl chloride, has been noted. These bags are used in the meat packaging industry.

VDC has a wide application as a barrier coating for paper and plastic films. Saran latexes have been developed which form an extremely water-resistant coating. This coating also provides the heat-seal characteristics of Saran. Other applications of these latexes include mixing in cement to produce high-strength mortars and concretes, and as binders for paints and nonwoven fabrics providing both water resistance and nonflammability (1).

VDC polymer lacquers are also used in coating films and paper. The lacquers are used mainly in food packaging where the features of inertness, lack of odor or taste, and nontoxicity are needed. The lacquers have also been applied as interior coatings for ship tanks, railroad tank cars, fuel storage tanks, and for the coating of steel piles and structures. The chemical resistance and good adhesion of the lacquers have made them an excellent long-term coating. The adhesive property also makes the lacquers a good binder for oxide pigmented coatings of magnetic tapes (1).

VDC is used to produce fibers. Monofilaments, made by extruding the copolymer, are used in the textile industry as furniture and automobile upholstery, drapery fabric, outdoor furniture, venetian-blind tape, and filter cloths (1). VDC is also used as a comonomer in the production of some modacrylic fibers such as Eastman Chemicals' Verel® and Monsanto's SEF® (1).

VDC copolymer plastics are produced by molding and extrusion of copolymer resins. The products provide chemical resistance and long service life. Uses of the plastics include gasoline filters, valves, pipe fittings, containers, chemical process equipment, tubing, and pipe liners (1).

Table 6 lists companies utilizing VDC for various ends (6). The total amount of VDC available for these uses is 18 x 10^3 metric tons/yr. Plant locations where vinylidene chloride is processed are shown in Figure 2.

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(7) Chemical Origins and Markets, Fifth Edition. G. M. Lawler, ed. Chemical Information Services, Menlo Park, California, 1977. 118 pp.

TABLE 6. CONSUMPTION AND END USE OF VINYLIDENE CHLORIDE (1974) (3)

Product	Company	Location	Capacity, metric tons/yr	Amount of vinylidene chloride monomer used, metric tons/yr	End use
PVDC[a] latex	Dewey and Almy Chemical	Owensboro, KY	4,500	4,000	Barrier coatings (coatings for glassines, paper, paperboard, polypropylene, and polyester film)
	Morton Chemical Co.	Ringwood, IL	1,600	1,400	
	BASF - Wyandotte	South Kearny, NJ	830	750	
	Staley Chemical	Lemont, IL	830	750	
	Dow Chemical	Midland, MI	830	750	
	Olin	Pisgah Forest, NC	200	180	
	DuPont	Circleville, OH	200	180	
		TOTAL	8,990	8,010	
PVDC latex	Dow Chemical	Midland, MI Allans Point, CT Dalton, GA Freeport, TX	6,800	3,400	Miscellaneous applications
	Goodrich Chemical	Avon Lake, OH	-[b]	-	
	Rohm and Haas	Knoxville, TN Bristol, PA	-	-	
	Standard Brands Chemical Industries	Cheswold, DE Kensington, GA	-	-	
	National Starch and Chemical Corp.	Merdosia, IL	-	-	
		TOTAL	13,600	6,800	
PVDC synthetic fibers	Tennessee Eastman	Kingsport, TN	-	-	Fabrication
	Monsanto Co.	Decatur, AL	-	-	
	American Cyanamid	Pensacola, FL	-	-	
		TOTAL	-	2,000	
PVDC-coated cellophane	DuPont	Richmond, VA	-	-	Fabrication
		Clinton, IA	-	-	
	Olin	Tecumseh, KS	-	-	
		Pisgah Forest, NC	-	-	
		Covington, IN	-	-	
	FMC	Fredricksburg, VA	-	-	
		Marcus Hooks, PA	-	-	
		TOTAL	-	-	
Extruded PVDC products	Cryovac	Simpsonville, SC	-	-	Fabrication
		Cedar Rapids, IA	-	-	
		Camarillo, CA	-	-	
		Iowa Park, TX	-	-	
	Oscar Meyer	Madison, WI	-	-	
		Chicago, IL	-	-	
		Davenport, IA	-	-	
		Philadelphia, PA	-	-	
		Nashville, TN	-	-	
		Vernon, CA	-	-	
	Dow Chemical	Midland, MI	-	-	
	American Can Co.	Cleveland, OH	-	-	
	Amtech, Inc.	Odenton, MD	-	-	
	Union Carbide Corp.	Centerville, IA	-	-	
		TOTAL	20,000	-	

[a] Polyvinylidene chloride.

[b] Dashes indicate data unknown.

Figure 2. Geographic distribution of plants that process vinylidene chloride.

SECTION 4

ENVIRONMENTAL SIGNIFICANCE AND HEALTH EFFECTS

ENVIRONMENTAL SIGNIFICANCE

Emissions arise during the production, use, and transportation of VDC. One estimate indicates that 1.8×10^3 metric tons of VDC were lost to the air in 1974 (2). A more recent publication states that 1×10^3 metric tons are released per year (3).

VDC Emissions During Production

Process points where VDC emissions occur include vents from the separator, finishing column, recycling tower, and storage tanks. VDC can be emitted from process wastewater and fugitive sources. Air from process vents may contain up to 5% VDC monomer. Possible fugitive and wastewater sources include 1) loading, unloading, and storage of VDC; 2) leaks from pumps, compressors, valves, and agitators; 3) pipe and equipment flanges and manhole cover seals; 4) opening equipment for inspection and maintenance; 5) sampling for laboratory analysis; 6) VDC in process water exposed to atmosphere; and 7) manual venting of equipment (2).

It has been estimated that 1.5×10^3 metric tons of VDC are emitted annually during production, principally through purification and recycle vents. This estimate, however, assumes there is no use of control technology, and therefore should be considered as an upper bound (2).

The heavy ends, composed of phenolic inhibitor and unreacted 1,1,2-trichloroethane, are removed from the finishing column and processed through a recycle tower (2). Phenolic inhibitor and 1,1,2-trichloroethane are drawn off and recycled while tower bottoms are disposed of as waste. Wastewater streams are discharged from the reactor, separator, and recycling tower (2). Effluent streams are also produced during tank car and storage tank washings.

Product Storage and Transportation

Vinylidene chloride is stored in the absence of light at -10°C and 69 kPa (2). Storage tanks are lined with nickel, baked phenolic, or glass, since the monomer may be corrosive or

unstable when contacted with steel (2). A layer of nitrogen is placed over the monomer to prevent contact with air or water which may cause undesirable polymerization.

Vinylidene chloride is transported by tank cars, tank trucks and barges (2). Jumbo tank cars, having 76 m^3 capacities, are the most common means of transport.

Pollution Potential from VDC Consumption and Use

PPG Industries, Inc., hydrochlorinates VDC to produce methyl chloroform. The reaction is represented as (8):

$$CH_2=CCl_2 + HCl \rightarrow CH_3CCl_3$$

This reaction is ideally conducted in the liquid phase with a catalyst such as ferric chloride. The reaction is carried out at 25°C to 30°C under slightly superatmospheric pressure. The product is continuously removed from the hydrochlorination step and is purified by fractional distillation, then dried, and stabilizers added to make it suitable for commercial use (8). Potential sources of gaseous VDC emissions exist throughout the process. Wastewater streams are also produced which may contain VDC and other materials.

The polymerization of VDC is another source of emissions. Both emulsion and suspension addition polymerization processes are used to produce polyvinylidene chloride latex and resin. Figures 3 and 4 give block diagrams for Saran resin production by the emulsion and suspension processes. VDC emissions arise at all steps of the polymerization. In both processes, the VDC monomer is washed to remove the inhibitor. During the reaction, the material is agitated. When the reaction is complete, the residual monomer is removed by flashing in vertical tanks and steam stripping in single or multiple stages. Fugitive emissions of the monomer may occur from leaks in equipment, agitators, vents, valves, and rupture discs. A liquid waste stream results from water-washing of the monomer feedstock to remove the inhibitor. The wastewater loading for polyvinylidene chloride is estimated to be 4.2 m^3/metric ton product. Additional liquid waste may result from leaks in the equipment. Another source of emissions is the cleaning of the reactors, accomplished by removal of solid deposits or by washing down the side with solvent or high-pressure steam (2).

In the drying stage of these processes, gaseous emissions of VDC and other low boiling compounds may result. Wastewater is produced from the dryers containing VDC and chemical additives.

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(8) Faith, Keyes, and Clark's Industrial Chemicals, Fourth Edition. F. A. Lowenheim and M. K. Movan, eds. John Wiley and Sons, New York, New York, 1975. pp. 837-838.

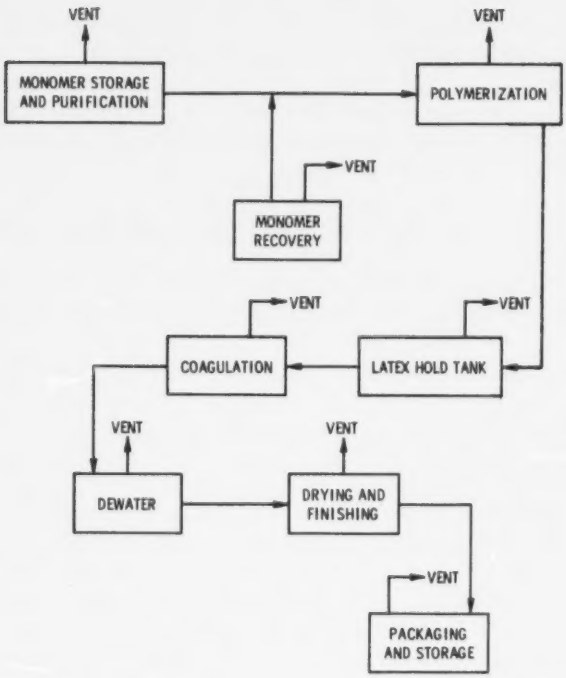

Figure 3. Saran emulsion process (2).

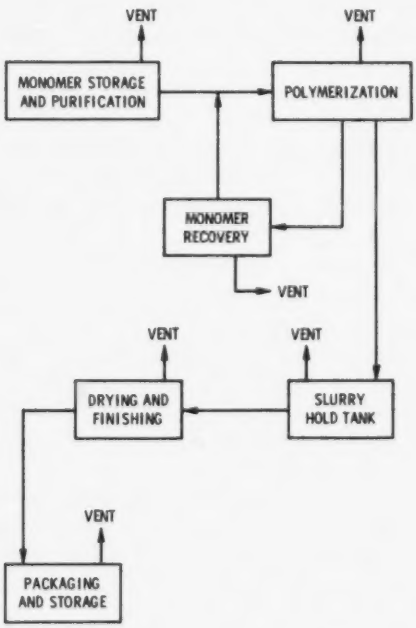

Figure 4. Saran suspension process (2).

In the suspension addition process, contaminated wastewater streams are produced from the centrifugation and filtration operations. Particulate emissions may arise from dusting in the dryers. In the final product preparation using suspension addition polymerization, the devolatilization procedure may cause gaseous emissions of VDC. Particulates may be emitted from pelletizing and bagging. Also, the extrusion of the polymer may produce a wastewater stream from quenching (2). There are no estimates of the levels of unreacted monomer emitted in the polymerization process. However, one EPA report estimates that as much as 25% of the VDC used in any given Saran production run is disposed of in landfill mainly in polymerized form (2).

Table 7 summarizes the estimated annual emissions of VDC from various sources in the United States.

TABLE 7. ESTIMATED ANNUAL EMISSIONS OF VINYLIDENE CHLORIDE IN THE UNITED STATES (2)

Source	VDC emissions, metric tons/yr
Monomer synthesis	1,500[a]
	280[b]
Polymer synthesis:	
Latex for burner coatings	54
Latex for miscellaneous coatings	68
Synthetic fibres	73
Coating resin for cellophane	82
Extrusion resin (emulsion)	12
Extrusion resin (suspension)	18
TOTAL	308
Fabrication polymer processing:	
Coating cellophane	0.7
Coating plastics, paper and glassine	7.4
Extrusion	0.2
Miscellaneous coating	5.4
TOTAL	14
TOTAL	1,840[c]

[a] Emissions using an existing control technology.

[b] Emissions reflecting new control technology at PPG plant by late 1975.

[c] Total of uncontrolled emissions.

Population at Risk

Worker exposure has generally not been monitored in the past. Tests have shown that 20,000 ppm can easily be reached in the proximity of a spill. In some cases, past worker exposures to VDC may have exceeded those of vinyl chloride, which were measured at 300 ppm to 1,000 ppm before OSHA limits were imposed (6).

To estimate the number of persons who may be exposed to VDC emissions, the population in a 5-mile radius around each plant listed in Table 6 and Table 5 has been determined (6). Approximately 3.5 million persons reside within this area near plants which either synthesize or polymerize VDC and/or fabricate materials based on VDC (Table 8) (6).

TABLE 8. ESTIMATED POPULATION AROUND VDC PLANTS (6)

Process	Number of persons
Monomer synthesis	89,000
Polymer synthesis	605,000
Fabrication	2,880,000
TOTAL	3,574,000

HEALTH EFFECTS

Exposure to either vapor or liquid VDC may be harmful. VDC has a moderate vapor toxicity (9). The exposure to high vapor concentrations of VDC results mainly in central nervous system depression and the associated symptoms of drunkenness. VDC has a characteristic mild, sweet odor resembling carbon tetrachloride or chloroform. A definite odor can be detected by most people at 1,000 ppm in air although some people detect the odor at 500 ppm. A disagreeable odor can be detected in vapors containing decomposition products at less than 500 ppm (9).

The odor or irritating property is usually inadequate to warn of overexposure. A drunkenness is rapidly produced with a single exposure of a few minutes to a high concentration of VDC (in the order of 4,000 ppm). Continued exposure at this concentration

(9) Irish, D. C. Aliphatic Halogenated Hydrocarbons. In: Industrial Hygiene and Toxicology, D. W. Fassett and D. D. Irish, Eds. Interscience Publishers, New York, New York, 1962. pp. 1305-1307.

may cause unconsciousness. Prompt and complete recovery from the anesthetic effects is usually observed if the exposure is of short duration. Prolonged exposure or repeated short-term exposures may be dangerous even if the vapor concentrations are too low to cause drunkenness. Organic injury may occur to the kidneys and liver. It has been recommended that the vapor concentration of VDC be below a time-weighted average of 25 ppm for repeated exposures (8 hr/day, 5 days/wk). Injury should not result from a single exposure of about 1,000 ppm for up to one hour or 200 ppm for up to eight hours (1).

Liquid VDC is irritating to the skin and eyes. Skin irritation has been noted after only a few minutes of contact; prolonged contact can cause first degree burns (2). This irritation may be partially due to the inhibitor (MEHQ or phenol) used in VDC to prevent polymerization.

Injury from skin absorption of the amount of phenol used in inhibited VDC appears to be unlikely. Inhibited VDC is moderately irritating to the eyes and will cause pain and conjunctival irritation and, possibly, some transient corneal injury and iritis (2).

VDC has recently been reported to cause liver impairment. At the BASF Wyandotte VDC polymerization plant in South Kearny, New Jersey, 27 of 46 workers examined showed 50% or greater loss in liver function. Other examinations indicate that VDC is biochemically altered in the body and may form intermediates similar to the cancer-producing metabolites of vinyl chloride (10).

VDC is a suspected carcinogen (3). Inhaled VDC is reported to produce liver tumors in rats at 200 ppm. Inhalation experiments with animals showed that VDC causes liver and kidney damage. When rats were pre-exposed to vinyl chloride and then tested with VDC, the acute toxicity of VDC was greatly enhanced. Concurrent exposure with vinyl chloride reduces the acute effects and may potentiate the carcinogenic effects. This is important because a significant part of polymer production involves the use of both chemicals (2). Acute toxicity data is given in Table 9.

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(10) Summary Characteristics of Selected Chemicals of Near-Term Interest. EPA-560/4-76-004 (PB-253 817), U.S. Environmental Protection Agency, Washington, D.C., April 1976. 50 pp.

TABLE 9. ACUTE TOXICITY OF VINYLIDENE CHLORIDE (3)

Lowest toxicity[a]	Dosage	Animal	Route
Lethal dose	3,700 mg/kg	Rabbit	Subcutaneous
	5,750 mg/kg	Dog	Oral
	225 mg/kg	Dog	Intravenous
Lethal concentration	10,000 ppm	Rat	Inhalation

[a] Known to cause death.

SECTION 5

CONTROL TECHNOLOGY

WORKSPACE ENVIRONMENT

Vinylidene chloride is a toxic and volatile chemical requiring careful handling and storage during its synthesis or polymerization. To avoid worker exposure to VDC, spills should be cleaned up immediately, equipment periodically inspected, and leaks repaired (11).

There are no specific government regulations concerning VDC emissions from monomer synthesis or processing. Several methods are available, however, to control vinylidene chloride emissions during monomer production, storage, and transportation. The efficiencies and costs of the control methods described were not available for this report.

PROCESS VENTS

Vents are located on the separator, finishing columns, recycling tower, and storage tanks of a VDC production facility (2). VDC emissions are ducted from the vents to activated carbon adsorbers where VDC is removed. Industry has not found it economically feasible to regenerate spent carbon thus requiring its disposal as a waste product.

VDC RECOVERY

Vinylidene chloride can be recovered from gas purging operations by refrigerated solvent scrubbing (2). Solvents which have been used for this control technique are acetone, methyl ethyl ketone, ethylene dichloride, butyl acetate and heptyl butyl ketone. Recovered vinylidene chloride is returned to the process system while the purge gases are being cleaned of VDC.

ORGANIC WASTE INCINERATION

Incinerators are generally used to dispose of flammable liquid wastes produced during VDC synthesis (2). Process air streams

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(11) Vinylidene Chloride Monomer, Physical Properties and Handling Precautions. Dow Chemical Company, Coatings Technical Service, Midland, Michigan.

may be vented to the incinerator to control hydrocarbon emissions.

STORAGE TANK EMISSIONS

Emissions from storage tanks may be controlled by other refrigerated vent recovery systems or by venting storage tank emissions to the main process stream. Vinylidene chloride is then recovered and the inerts are removed along with production wastes (2).

CURRENT INDUSTRY EFFORTS

The VDC industry is adopting control procedures for vinylidene chloride which parallel those for vinyl chloride (2). The type of control technology used in controlling vinyl chloride emissions could be applicable to VDC. Suggested control measures for VDC from existing vinyl chloride technology are given in the following paragraphs.

The emissions from pump, compressor, and agitator seals can be controlled by installing double mechanical seals and maintaining a liquid between the seals at sufficient pressure to cause the liquid to leak into the pump should the seal fail.

VDC that is present in equipment that is to be opened for maintenance or inspection can be vented to a control device by purging the equipment with an inert gas such as nitrogen or displacing the contents with water before it is opened.

The emissions occurring during loading and unloading from the loading area lines can be controlled by purging the lines to a control device such as an incinerator or carbon adsorption unit. The emissions from slip gauges can also be vented to a control device.

Emissions from leaking pressure relief valves can be reduced by installing leak proof rupture discs upstream of the relief valve.

Emissions resulting from sampling for laboratory analysis can be virtually eliminated by letting the gas that is to be sampled flow through the sample flask to a lower pressure point in the process. The sample flask can then be blocked off and any VDC that remains in the sample lines can be purged to a control device before the sample flask is removed.

Many fugitive sources can be monitored with a formal program of leak detection and repair. The detection can be accomplished with both fixed point and portable monitoring devices. Using methods described above, fugitive emissions could be reduced by 90%.

VDC can be stripped from the inprocess wastewater, and transferred to a control device, such as an incinerator or adsorber; VDC could possibly be recovered from the adsorber.

VDC that is present in the polymerization reactors can be displaced to the monomer recovery system for reuse by filling the reactor with water before it is opened for cleaning, maintenance, or inspection.

The need to open the reactors for cleaning can be reduced by cleaning the reactor while it is closed with high pressure water sprays, circulating an organic solvent through the reactor to dissolve any solids that may have accumulated and by a combination of recipe reformulation and reactor design to reduce scale formation.

Polymerization reactor safety valve discharges can be avoided by instrumenting each reactor with a pressure or temperature alarm to alert the operator to take appropriate action. This could include venting the reactor contents to a gasholder where the VDC can be recycled, or injecting certain chemicals into the reactor to stop the reaction and prevent further pressure build-up. During power failure, these chemicals could be added manually by hydraulic injection systems.

VDC that is present in all captive or point sources in the monomer and polymer plants can be controlled by adsorption on activated carbon, by absorption in an organic solvent, or by incineration. For vinyl chloride, each of these techniques can reduce the vinyl chloride content of the gas being treated to less than 10 ppm.

Control levels equivalent to the "add-on" devices discussed above can be achieved in certain point sources in the polymerization process by stripping the slurry leaving the reactors of the residual, unreacted VDC. These sources, which are downstream of the stripper, include the slurry blend tanks, the centrifuges, the dryers, and the bulk resin storage areas.

It is difficult to estimate the emissions reduction and costs of these control strategies as applied to VDC. Control test data and cost estimates for vinyl chloride are available in EPA's publication on the Emission Standard for Vinyl Chloride (12).

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(12) Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride. EPA-450/2-75-009, U.S. Environmental Protection Agency, 1975. 536 pp.

SECTION 6

REGULATORY ACTIONS IN PROGRESS

The American Conference of Governmental Industrial Hygienists has established a threshold limit value of 10 ppm (13). Vinylidene chloride has recently been reported to cause liver impairment. Workers examined at the BASF Wyandotte VDC polymerization plant in South Kearny, New Jersey showed a 50% or greater loss in liver function. Other studies have indicated that VDC is biochemically altered in the body and may form intermediates similar to the cancer-producing metabolites of vinyl chloride (10).

NIOSH is planning to monitor the follow-up studies on workers at the South Kearny BASF plant and will survey other VDC production sites in 1977 to determine if a workplace standard should be recommended (10).

EPA is preparing an assessment of the air pollution problems associated with VDC production and use. Fetotoxicity and embryotoxicity have been demonstrated under EPA-funded contracts. Data on environmental effects of VDC are also being obtained (10).

A preliminary air pollution assessment of VDC indicates that regulation under Sections 111 and 112 of the Clean Air Act is not warranted at this time (14). VDC has been designated as a priority pollutant for study under the Federal Water Pollution Control Act.

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(13) TLV's® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1975. American Conference of Governmental Industrial Hygienists. Cincinnati, Ohio, 1975. 97 pp.

(14) Identification of Selected Federal Activities Directed to Chemicals of Near-term Concern. EPA-560/4-76-006, U.S. Environmental Protection Agency, Washington, D.C., July 1976. 36 pp.

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